

UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP012139

TITLE: Nano-Sized [60]Fullerene-Cyclodextrin Molecules

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings. Volume 675.
Nanotubes, Fullerenes, Nanostructured and Disordered Carbon. Symposium
Held April 17-20, 2001, San Francisco, California, U.S.A.

To order the complete compilation report, use: ADA401251

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP012133 thru ADP012173

UNCLASSIFIED

Nano-Sized [60]Fullerene-Cyclodextrin Molecules

Jeong-Seo Park, Han-Chang Kang, and Kurt E. Geckeler*

Laboratory of Applied Macromolecular Chemistry,
Department of Materials Science and Engineering,
Kwangju Institute of Science and Technology,
1 Oryong-dong, Buk-gu,
Kwangju 500-712, South Korea

ABSTRACT

As [60]fullerene is a very hydrophobic macromolecule, there have been a number of attempts to make it more hydrophilic for biomedical applications. By attaching hydrophilic moieties such as poly(oxyethylene)(POE) chains and cyclodextrin molecules to [60]fullerene, novel water-soluble and biocompatible materials have been successfully prepared [1,2].

The synthesis of novel macrocyclic fullerene conjugates which are water-soluble is reported. The telechelic fullerene derivatives have been prepared *via* addition reaction of POE-based arms with covalently bonded β -cyclodextrin (CD) to [60]fullerene. To this end, a mono-tosylated CD derivative has been prepared in pyridine and then reacted with an amino-functional POE in the presence of triethylamine. The subsequent reaction of [60]fullerene with the hydrophilic POE-conjugated CD-derivative yielded the macrofullerene after separation and purification procedures.

The macrocyclic [60]fullerene derivatives obtained were soluble in water and characterized by UV-VIS and FT-IR spectroscopy as well as light scattering measurements and thermogravimetric analysis.

INTRODUCTION

Since [60]fullerene has been made preparatively accessible [3], the promising properties of [60]fullerene stimulate an increasing interest for fullerene-containing polymers in view of biomedical applications [1,2]. There have been a number of attempts to make it more hydrophilic, as [60]fullerene possesses radical scavenging effects [4].

POE exhibits the minimal interfacial energy in an aqueous environment and an unique solubility in water. Furthermore, as POE is a very hydrophilic and biocompatible material, it is already applied in many fields such as biomedical and pharmaceutical areas [5]. And CD are water-soluble cyclic oligosaccharides built up of glucopyranose units. Thus, by using of [60]fullerene as a molecular core in linking multiple POE chains and CD molecules novel water-soluble and biocompatible materials have been successfully prepared.

EXPERIMENTAL DETAILS

The synthetic procedure consists of three steps. The first step is the preparation of mono-6-(p-tolylsulfonyl)- β -cyclodextrin (m-TsCD). m-TsCD was synthesized by following a standard procedure [6].

The second step was the preparation of mono-poly(oxyethylene)- β -cyclodextrin (POE-CD). It was synthesized by reacting equimolar quantities of m-TsCD and difunctional amino POE (aPOE) with a molecular mass 2 kg mol^{-1} .

In the final step, we synthesized the (aPOE)-poly(oxyethylene)- β -cyclodextrin (F-(POE-CD)_n) by reacting with POE-CD and [60]fullerene. During the reaction, the color of solution changed from purple to light-yellow, and then to pink.

UV/Vis spectra were obtained with a UV/Visible spectrometer (Perkin Elmer, Lambda 12). The particle size was measured by dynamic light scattering (Malvern Instruments Ltd. Series 4700) with argon ion laser system at 488 nm with a digital correlator.

RESULTS AND DISCUSSION

The macrocyclic [60]fullerene derivatives obtained were soluble in water and the synthesis of these conjugates was confirmed by UV-VIS Spectroscopy.

In Figure 1. it is shown that the [60]fullerene-POE conjugate absorbs in the UV-visible region showing a maximum at 250-270 nm. At higher wavelengths, the absorbance presents a smoothly decreasing shoulder without characteristic maxima. As the reaction proceeded, the peak height at around 340 nm decreased and finally disappeared. This phenomena explains the disruption of the π -bonds of [60]fullerene due to the formation of side arms which are covalently bonded to [60]fullerene.

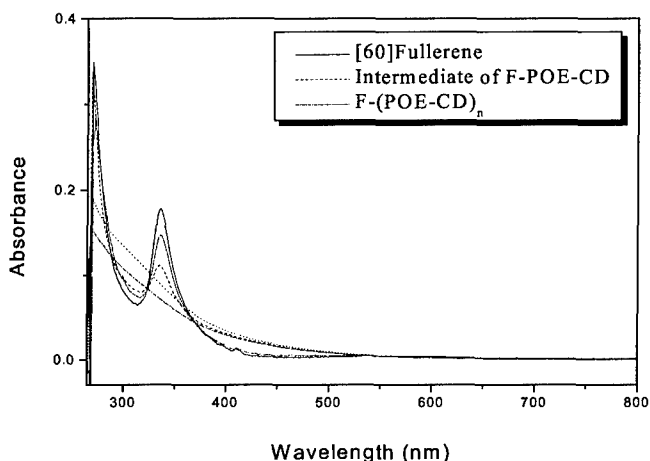


Figure 1. UV/VIS spectra showing the formation of [60]fullerene-cyclodextrin conjugates (F-(POE-CD)_n) by an addition reaction with reaction time

The infrared spectrum of the polymer is shown in Figure 3. It looks similar to that of the POE-CD prepolymer. A broad band around 3440 cm^{-1} corresponding to the absorption of primary and secondary amine and alcohol groups of CD is shown. It also shows a sharp peak at around 1100 cm^{-1} . Interestingly the two peaks around 520 cm^{-1} and 570 cm^{-1} , shown in both [60]fullerene and POE-CD, changed their forms to broad bands.

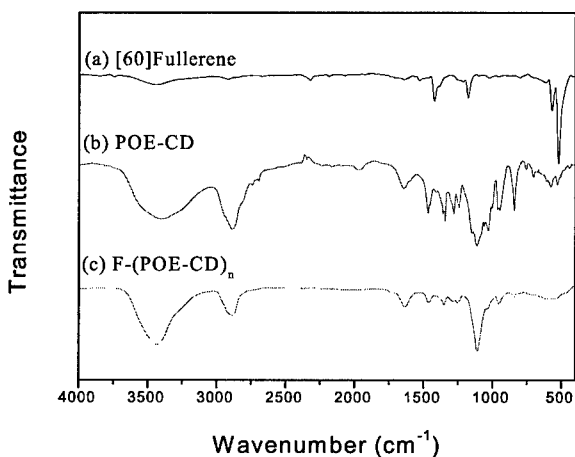


Figure 2. FT-IR spectra of (a) [60]fullerene , (b) POE-CD, and the reaction product (c) F-(POE-CD)_n

Figure 3 shows the particle size distribution of F-(POE-CD)_n obtained by laser light scattering. The molar mass thus obtained was 13,496 g mol⁻¹ and the average particle size in water was 24.6 nm with a mean value distribution of 98.7%. This value is a little smaller than the expected whole length of fully extended fullerene derivatives. Based on the thermogravimetric analysis, an average number of 2.07 side-arms could be calculated.

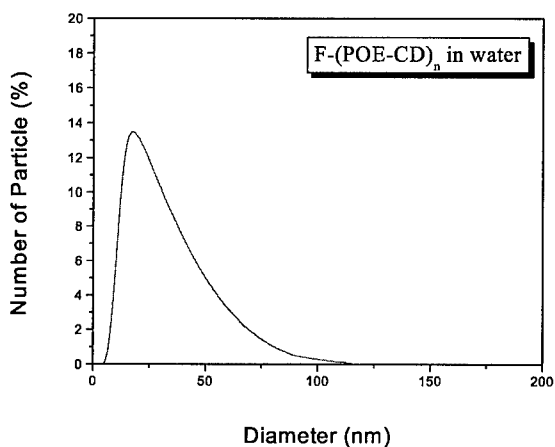


Figure 3. Particle size distribution of F-(POE-CD)_n by laser light scattering

The characteristic properties such as hydrophilicity and expected biocompatibility of this novel macrocyclic molecules hold promise for a broad range of biomedical applications [7,8].

CONCLUSIONS

The synthesis of a novel water-soluble macrocyclic [60]fullerene conjugate is described. The macromolecules were prepared by the multiple addition of POE arms with covalently bonded CD to [60]fullerene. The preparation of the [60]fullerene conjugates by the addition of hydrophilic POE and CD is a useful method of imparting water-solubility of [60]fullerene derivatives.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Samal and Dr. Murthy for helpful discussions. This study was financially supported by the Ministry of Health and Welfare of Korea (HMP-00-B-31400-0164).

REFERENCES

1. K. E. Geckeler, *Trends Polym. Sci.*, **2**, 355 (1994)
2. K. E. Geckeler and S. Samal, *Prog. Rubber Plast. Technol.*, **16**, 69 (2000).
3. H. W. Kroto, J.R.Heath, S. C. O'Brian, R. F. Curl and R. F. Smally, *Nature*, **318**, 162 (1985).
4. K. E. Geckeler and S. Samal, *Fullerene Sci. Technol.*, **9**, 17 (2001)
5. S. Herman, G. Hooftman and E. Schacht, *J. Bioact. Compat. Polym.*, **11**, 135 (1996).
6. T. Nazaki, Y. Maeda, K. Ito, and H. Kitano, *Macromolecules*, **28**, 522 (1995).
7. K. A. Connors, *Chem. Rev.*, **97**, 1325 (1997).
8. K. E. Geckeler and S. Samal, *Polym. Internat.*, **48**, 743 (1999).